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STUDY OF IMPROVED BERYLLIUM
OXIDE MATERIALS FOR MICROELECTRONICS
TECHNOLOGY

Final Report

Contract NASw-685

National Beryllia Corporation
Haskell, New Jersey

STUDY OF IMPROVED BERYLLIUM OXIDE MATERIALS FOR MICROELECTRONICS TECHNOLOGY

Final Report for the Period
8 April 1963 through 8 December 1963
Contract NASw-685

Submitted by
National Beryllia Corporation
Haskell, New Jersey

to
National Aeronautics and Space Administration
Washington 25, D. C.

31 December 1963

FOREWORD

This is the final report prepared by National Beryllia Corp. under Contract NASw-685 for National Aeronautics and Space Administration. The objectives of the work have been to develop techniques for the growth of single crystals of beryllium oxide suitable for use in microelectronic applications, and the precise determination of their mechanical, thermal and dielectric properties. The work was administered under the direction of the Electronics and Control Division, National Aeronautics and Space Administration.

This report covers work carried out by the Research and Development Division of National Beryllia Corp., between 8 April 1963 and 8 December 1963.

Research was directed by Dr. Eugene Ryshkewitch, with Philip S. Hessinger as Project Manager. Technical personnel participating in the program included R. L. Sharkitt, K. H. Styhr, G. Ferment and W. Allen.

ABSTRACT

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Single crystals of beryllium oxide have been grown by the water-vapor transport method, evaporation-condensation technique, and crystallization from molten salts. Hexagonal shaped platelets of monocrystalline BeO have been produced, mainly by the water-vapor transport method, in sizes up to 0.175" diameter, with average diameters of 0.050-0.060". Chemical purity of these crystals has been very high, with most of the impurities concentrated at the surfaces. High levels of purity have also been maintained on monocrystalline products of the evaporation-condensation and molten salts techniques.

Dielectric, optical and thermal properties of single crystals of BeO have been measured, and results correlated with crystal structure. Results of experimental work have shown strong indications that monocrystalline BeO exhibits many characteristics, both physical and mechanical, which make the material far more attractive than the polycrystalline variety. The use of monocrystalline BeO, preferentially aligned, shows promise of far superior particulate and aggregate properties for applications as window, filter, and controlled energy transfer materials.

Author

TABLE OF CONTENTS

List of Figures

List of Tables

I. INTRODUCTION

The unique combination of two physical properties have made beryllium oxide far more attractive than other refractory crystalline materials. Beryllium oxide exhibits both an extremely high thermal conductivity and at the same time is a dielectric having high electrical resistivity and low dielectric loss. Sintered beryllium oxide has, therefore, been useful in numerous advanced electronic applications where heat dissipation from active components is of critical importance. In polycrystalline form, produced by normal cold pressing and sintering operations to yield a high purity body with 95-98% of theoretical density, beryllium oxide exhibits a thermal conductivity of 0.63 cal/cm^2/cm/sec°C at room temperature, with electrical resistivity of at least 10^{15} ohm/cm and dielectric loss tangent of 0.0004 or less depending on frequency. A list of some physical properties may be found in Figure 1.

The thermal and dielectric properties of polycrystalline BeO are well known as well as the basic crystal structure of the material. Several investigators have reported on the piezoelectric and ferroelectric properties of BeO. The objectives of the present program have been the development of techniques for the growth of single crystals of beryllium oxide suitable for use in microelectronic applications, and the precise determination of their mechanical, thermal and dielectric properties. Properties of specific interest in BeO single crystals are:

a. Thermal conductivity in "a" and "c" crystallographic directions
b. Electrical resistivity as a function of temperature
c. Dielectric constant as a function of frequency and temperature
d. Dielectric loss as a function of frequency and temperature
e. Infrared energy transmission
f. Optical properties
g. Crystal structure.

Figure 1

SOME PHYSICAL PROPERTIES OF CRYSTALLINE BERYLLIUM OXIDE

Crystal Structure: Hexagonal: Wurtzite (ZnS)

Lattice Constants:	20°C	1025°C
	ao = 2.69 Å	2.72 Å
	co = 4.39 Å	4.43 Å
Molar Volume:	8.33	
Density:	3.008 gm/cc	
Melting Point:	2570 ± 30°C	
Boiling Point:	4120 ± 170°C	
Thermal Conductivity:	20°C	1000°C
(Cal/cm^2-sec-cm-°C)	0.63	0.07
Volume Resistivity	20°C	1000°C
(ohm-cm)	10^{15}	10^{7}

II. SURVEY OF PREVIOUS WORK

Several papers have been published based on work in the area of production of beryllium oxide powders and the growth of BeO crystalline powders by calcination of various salts such as acetates and oxalates. Beryllia crystals resulting from these studies have not been considered under the present research since they are extremely small in crystallite size and their end objective is utilization in fabrication of ceramic bodies.

Growth of beryllium oxide in single crystal form has been investigated by various groups including the present authors under programs related to nonelectronic applications. Ryshkewitch and associates (1) have reported on research and development in the growth of BeO whiskers to be utilized for high temperature resistant beryllia fiber reinforced structural composites. This work conducted under Air Force sponsorship led to techniques for the preparation of single crystal whiskers of elongated geometry by oxidation of beryllium metal vapors in a controlled atmosphere. Mechanical property measurements on such whiskers indicated strengths in the range of 800,000 to 1,900,000 psi in the a crystal direction and 100,000 to 500,000 psi in the c crystal direction. Work done within the same investigation led to preparation of such whiskers also by a high temperature water-vapor transport, generally yielding lath-like crystals of predominantly c axis orientation and hexagonal platelets of basal plane orientation. Austerman and Hopkins (2) have reported on the character of beryllium oxide crystals grown from alkali molybdate solution, principally Li_2MoO_4-MoO_3. Using this technique in a temperature range of 1400°C they obtained crystals up to 5 mm in the imperfect condition and up to 2 mm in a clear well-formed structure. Three dimensional crystals of both the pyramidal and the prismatic form were produced by varying the growth conditions. No attempt was made under this program to evaluate the properties of the material. Newkirk and Kingman [3] have reported on synthesis of beryllium oxide single crystals also utilizing growth from a molten flux. In their work crystals up to a maximum of 5 mm were obtained. Their study included some research on the water vapor transport technique, however, they were unable to adapt it to growth of larger crystals.

III. TECHNICAL PROGRAM

A. Objectives

The objectives of the present program have been the development of techniques for the growth of single crystals of beryllium oxide suitable for use in microelectronic applications, and the precise determination of their mechanical, thermal and dielectric properties.

1. Task A - Single Crystal Growth

The single crystal growth portion of the program has had as its main objective the perfection of techniques for reproducibly growing platelet type crystals of controllable high purity and minimum surface contamination and imperfections.

2. Task B - Dielectric, Optical and Thermal Properties

The thermal and dielectric properties of polycrystalline BeO are well known as well as the basic crystal structure of the material. Several investigators have reported on the piezoelectric and ferroelectric properties of BeO. The testing portion of this program has had as its main objective the precise determination of the anisotropic characteristics of single crystal BeO as evidenced by the orientation sensitivity of the mechanical, physical and thermal properties.

B. Approach

1. Task A - Single Crystal Growth

The nucleation and growth of pure single crystals of BeO has been attempted in two completely different environments. The first of these is by the water-vapor transport method where use is made of a pure BeO system wherein polycrystalline BeO is both the nutrient and seeding material. The second technique is by crystallization of BeO from molten alkali molybdate.

a. Water-Vapor Transport Method

Beryllium oxide single crystals can be grown from the vapor phase by taking advantage of the reversible characteristics of the reaction:

$$BeO + H_2O = Be(OH)_2$$

The reaction as written will begin at approximately 300°C. At temperatures approaching 1900-2000°C considerable amounts of material may be transported in the vapor state as beryllium hydroxide, using an appropriate carrier gas. Upon reaching a seed surface, under proper thermodynamic conditions, the beryllium hydroxide will decompose and condense as pure BeO crystals. While this process seems relatively simple and straightforward, it is in fact rather complex since many processing variables determine the quality and quantity of the BeO crystal yield.

The reaction chamber is made of all BeO but there is still a possibility of contaminating materials being released from the chamber walls as a result of corrosive attack by water vapor. The presence of vapor phase contaminants in the chamber may be strongly affecting the size to which a crystal may grow. Surface contamination of a growing crystal could be sufficient to upset the thermodynamic conditions conducive to continued growth. The presence of this contamiration on the surface can then prevent continued growth by not affording an effective nucleation activity. Some evidence has been seen supporting this type of reason.

Basically the growth apparatus consists of a sintered beryllium oxide cylinder, open at both ends, which serves as the reaction chamber when placed vertically in the graphite susceptor of an induction heating furnace. The reaction chamber is made completely of pure BeO components, and all other materials are isolated from the reaction chamber and transport path to insure a minimizing of contamination possibility. High fired beryllium oxide in form of chips or powder is introduced into the lower section of the reaction chamber, directly in the carrier gas inlet path, where it serves as nutrient material for the desired reaction. Helium is used as the carrier gas, and is passed through a high humidity chamber before entering the reaction chamber through a Berlox high purity BeO inlet tube. Reaction occurs between the water vapor and BeO nutrient charge. Reaction also occurs at the walls of the BeO reaction chamber. The product of these reactions, beryllium hydroxide-$Be(OH)_2$, is transported in the vapor state to the upper section of the reaction chamber where it decomposes and crystalline BeO condenses on the surface of BeO seeding substrates.

The results of the water-vapor transport experiments are listed in Table I and discussed in later sections of this report. Figures 2 and 3 describe the apparatus and reaction chamber components. Figs. 4 & 5 show single crystal products.

b. Growth from Solution

In order to obtain crystals of the non-platelet type, attempts were made to produce single crystals of BeO by crystallization from alkali molybdates. Basic equipment for this type of growth consists of an inert reaction vessel containing an alkali molybdate and nutrient BeO in an air firing furnace capable of maintaining the molten bath at a constant temperature while one region on the surface of the melt is artificially heat sunk to produce a controllable thermal extraction area.

Data indicate that at 1455°C approximately 0.25 moles of BeO may be dissolved in 1 mole of Li_2MoO_4:1.25MoO_3. Crystallization of BeO may then be accomplished at temperatures in the neighborhood of 1425°C.

A platinum wound furnace was first considered for this work but reaction between the MoO_3 vapors and the platinum wire caused continuous breakdown, and a decision was made to incorporate a glo-bar, muffled furnace instead. The Al_2O_3 furnace muffle was lined with a BeO tube to isolate the reaction region and to afford better control of the chamber temperature. The Li_2MoO_4, MoO_3 and BeO were all placed in a platinum crucible which was placed inside a Berlox BeO refractory boat. A thermal gradient was established by introducing a BeO rod into the melt and heat sinking the opposite end.

Table II lists the results of the crystallization experiments, and Figure 6 describes the apparatus. Results are described and discussed in later sections of this report.

TABLE I

WATER-VAPOR TRANSPORT EXPERIMENTAL CRYSTAL GROWTH RUNS

Run No.	Carrier Gas	Gas Flow Rate	Vaporizer Temp.	H_2O Flow Rate	Operating Temperature	Time at Temperature	Results
12	He	1 L/min	175°C		1900°C	2 hr 30 min	No crystals
13	He	1 L/min	170°C		1900	2 hr 30 min	Some crystal growth
14	He	1 L/min	175°C	1 cc/min	1900	2 hr 30 min	Fibers on exit end of reaction tube
15	He	1 L/min	170°C	1 cc/min	1850	2 hr 30 min	Some growth at ends of reaction tube
16	He	1 L/min	185°C	1 cc/min	1850	2 hr 30 min	Fibrous growth on rod numerous small platelets
17	He	1 L/min	185°C	2 cc/min	1800	2 hr 30 min	Good yield of platelets on seed rod

TABLE I (CONT'D.)

WATER-VAPOR TRANSPORT EXPERIMENTAL CRYSTAL GROWTH RUNS

Run No.	Carrier Gas	Gas Flow Rate	Vaporizer Temp.	H_2O Flow Rate	Operating Temperature	Time at Temperature	Results
18	He	1 L/min	175°C	2 cc/min	--	--	Sight Tube blocked Bad run.
19	He	1 L/min	160°C	2 cc/min	1800°C	2 hr 30 min	Slight growth on sharp edges. Fibrous growth in regions pre-treated with hydrofluorosilicic acid.
20	He	2 L/min	185°C	2 cc/min	1775°C	1 hr 30 min	Very good yield-Many platelets up to 3/16" across-Some discoloration. Best yield in region pre-treated with HF.
21	He	1 L/min	195°C	2 cc/min	1795°C	2 hrs	Poor yield-Difficulty with hot plate for vaporizer.
22	He	1 L/min	190°C	2 cc/min	1950°C	2 hrs	BeO reaction tube shifted. Some growth in regions pre-treated with HCL and HF.
23	He	1 L/min	180°C	2 cc/min	1795°C	2 hrs	Fibrous growth - No platelets.

TABLE II

SOLUTION GROWTH EXPERIMENTS

Run No.	Furnace Charge	Solution Temp.	Solution Time	Crystallization Temp.	Crystallization Time	Results
1	Li_2MoO_4(NBC):BeO 1 : 2	1450°C	24hrs.	1400°C	36hrs.	Undissolved
2	Li_2MoO_4(NBC):BeO 1 : 2	1495°C	24hrs.	1400°C	48hrs.	Partially dissolved No Crystallization
3	Li_2MoO_4(NBC):BeO:MoO_3 1 2 : 2	1460°C	36hrs.	1440°C	36hrs.	BeO partially dissolved. Some rejection of very small BeO crystals
4	$Li_2Mo_2O_7$:MoO_3:BeO 1 :1.25: 1	1460°C	24hrs.	1440°C	24hrs.	Discolored-Some dissolution. No crystallization
5	$Li_2Mo_2O_7$:BeO 1 :0.5	1460°C	36hrs.	1440°C	72hrs.	Partially dissolved No crystallization
6.	Li_2MoO_4(NBC):MoO_3:BeO 1 :1.25:0.5	1460°C	36hrs.	1445°C	48hrs.	Mostly dissolved Slight crystallization.
7	Li_2MoO_4(NBC):MoO_3:BeO :1.25:0.5	1455°C	36hrs.	1425°C	48hrs.	Mostly dissolved. Crystallization of small BeO platelets up to 0.005-0.010" long

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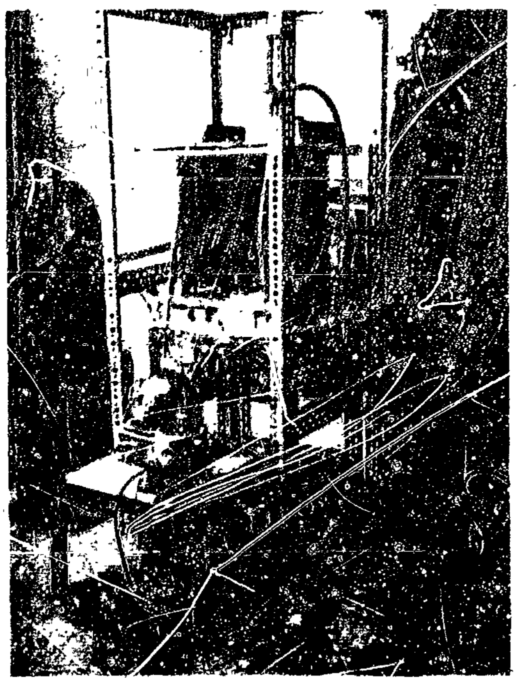


Figure 2 BERYLLIA CRYSTAL - GROWING APPARATUS SHOWING INDUCTION HEATER, CARRIER GAS TRAIN AND WATER VAPORIZER

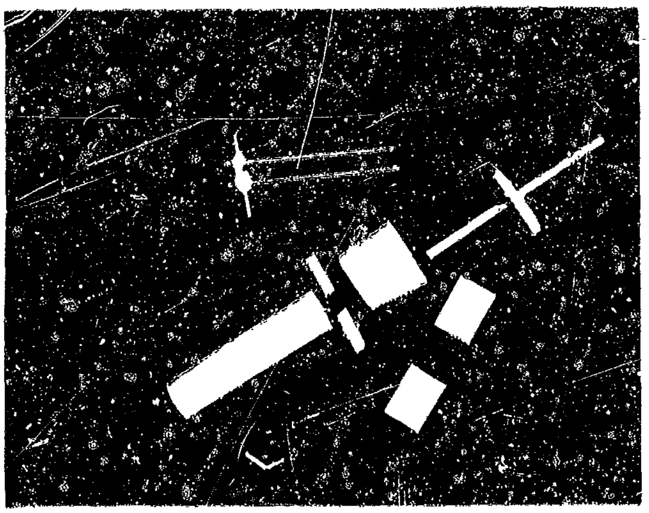


Figure 3 INTERNAL COMPONENTS OF APPARATUS; BeO REACTOR TUBE AND SEED RODS

Figure 4

BERYLLIA SINGLE CRYSTAL PLATELET SHOWING IMPURITY DROPLETS ON SURFACE (100X)

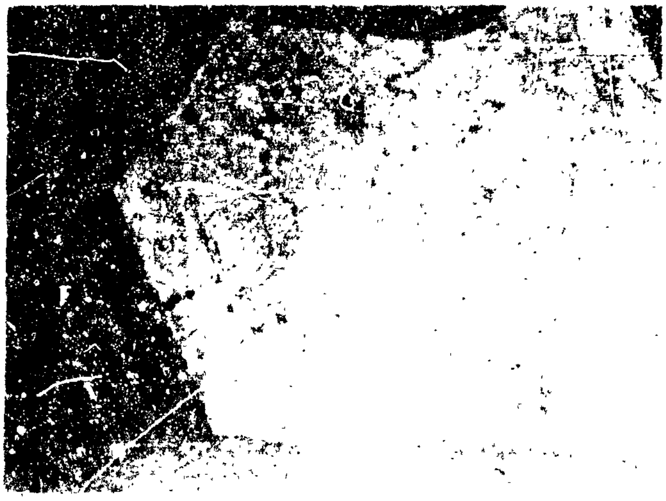


Figure 5

SAME AS ABOVE IN BRIGHT FIELD ILLUMINATION SHOWING IMPURITY MIGRATION TRACES (100X)

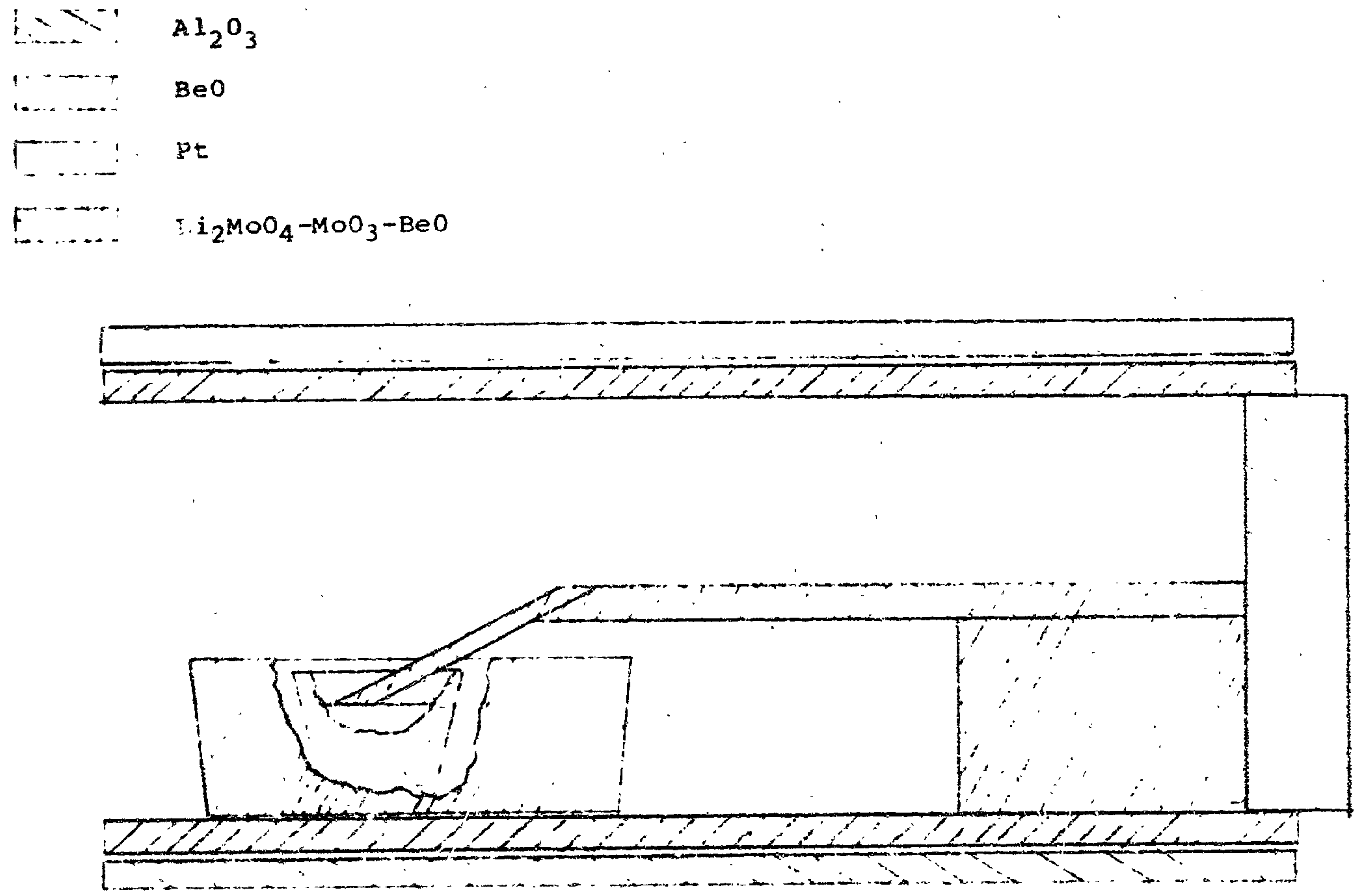


FIGURE 6 - Schematic of Solution Growth Apparatus Showing Controlled Thermal Extraction Facility

2. Task B - Properties Determinations

a. Dielectric

The basic equipment used for determination of dielectric properties includes a Federal Model H Teraohmmeter for DC resistivity, a General Radio Model 1615A capacitance bridge assembly and a Boontor Radio 160A Q-meter. Because of the characteristic brittleness and size of the crystal samples available, it was necessary to construct specially designed sample holders capable of making measurements of extremely fine gaps with reproducibility and precision. To achieve this, a preliminary sample holder (No. 1) was constructed and exploratory measurements made with the General Radio bridge in order to determine some of the problem areas in working with such a system. The results of these experiments are listed in Table III, and the sample holder is shown in Figure 7. Based on these results, the following requirements were established for such a measurement apparatus.

(1) Capability of adjustment and calibration of capacitance gap openings down to less than 0.0001" (2.5 microns).
(2) Complete flexibility in adjustment of probe and ground electrode location so as to allow measurement of not only platelet type materials but ultimately fibrous crystals.
(3) Facility for adapting the sample holder to high temperature measurements without disturbing the major electrical characteristics of the system.
(4) Design made such that the extremely small platelet crystals can be inserted and removed with a minimum of handling and with their location being such that they can be physically observed during test.

With these requirements in mind, sample holder No. 2, (Figure 8), was designed and constructed. Preliminary experiments were run using polycrystalline Berlox specimens of varying thicknesses, both with and without metallized surfaces. Calibration curves were thus generated to determine reproducibility and precision of measurements and effects of shielding. Calibration curves for sample holders No. 1 and No. 2 are shown in Figures 9 and 10. Data used in establishing the characteristics of these curves is listed in Tables IV and V.

As was to be expected, the selection and fabrication of electrodes was one of the more critical considerations in the establishment of conditions acceptable for dielectric testing. Crystal size, non-uniformity of crystal surface and brittleness can lend considerably to the difficulties involved in selecting and affixing electrodes. The first approach was to use silver

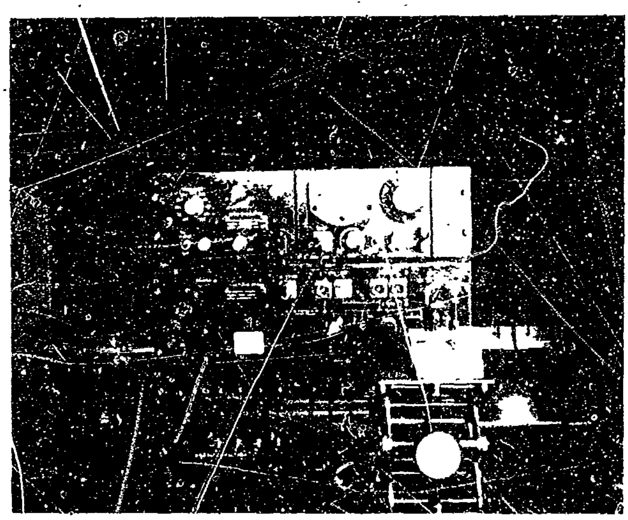


FIGURE 7

Capacitance Bridge Assembly with Crystal Sample Holder No. 1

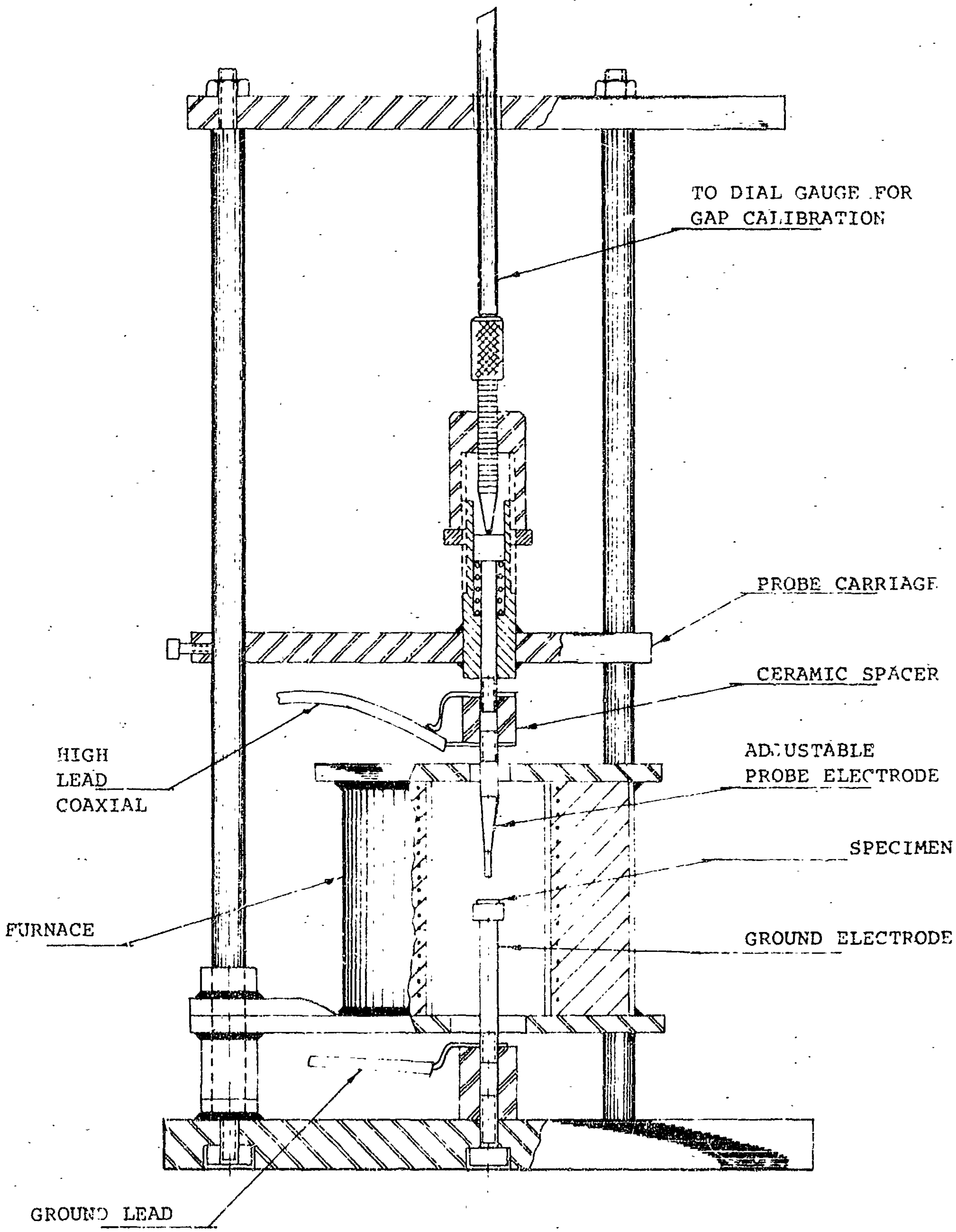


FIGURE 8

BeO CRYSTAL DIELECTRIC SAMPLE HOLDER NO. 2

TABLE III

PRELIMINARY DIELECTRIC MEASUREMENTS OF BERYLLIA SAMPLES AT 25°C

Sample Holder No. 1

Description of Sample	Frequency f	C_2 (Picofarads)	C_1 (Picofarads)	C_x (Picofarads)	D_2	D_1	Dielectric Constant K
(a) BeO Disc Type P-5 Metallized w/Ni Plate	1 KC	.7600	5.5200	4.7600	.0090	.0030	7.19
(b) BeO Disc Type P-5 Metallized w/Ni Plate	1 KC	.7500	5.3290	4.5790	.0090	.0030	6.90
(c) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7752	19.4000	18.6248	.0100	.0050	8.49
(d) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7780	17.7300	16.9520	.0096	.0100	7.85
(e) BeO Disc Type P-6 Metallized w/Cu Plate	1 KC	.7866	17.5900	16.8034	.0200	.0010	7.88
(f) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7686	1.1680	0.3994	.0100	.0100	8.09

Sample Holder No. 1 (Cont'd.)

Description of Sample	Frequency f	C_2 (Picofarads)	C_1 (Picofarads)	C_x (Picofarads)	D_2	D_1	Dielectric Constant K
(g) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7580	1.1940	0.4360	.0100	.0100	8.90
(h) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	.7749	1.1853	0.4104	.0100	.0120	8.42
(i) BeO Disc Type P-7 Metallized Mo-Mn only	1 KC	.7904	1.6176	0.8272	.0100	.0050	6.36
(j) BeO Disc Type P-7 Metallized Mo-Mn only	1 KC	.7740	1.5947	0.8207	.0100	.0050	6.31
(k) BeO Disc Type P-7 Metallized Mo-Mn only	1 KC	.7777	1.5818	0.8041	0.0100	.0050	6.41

Sample Holder No. 2 (Without Sample Shield)

Description of Sample	Frequency f	Picofarads C_2	Picofarads C_1	Picofarads C_x	Dielectric Constant K
(a) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	17.3700	17.7500	.3800	7.69
(b) BeO Disc Type P-3 Metallized w/Gold Plate	1 KC	17.3600	17.7600	.4000	8.18
(c) BeO Single Crystal	1 KC	--	18.9900	--	--

TABLE IV

CALIBRATION DATA FOR DIELECTRIC
SAMPLE HOLDER NO. 1

Electrode Spacing	Frequency	Capacitance	Dissipation Factor
0.0015"	1 KC	0.8700	0.0090
0.0025	1 KC	0.8600	0.0090
0.007	1 KC	0.8140	0.009
0.010	1 KC	0.8050	0.009
0.015	1 KC	0.7850	0.0097
0.020	1 KC	0.7770	0.0099
0.025	1 KC	0.7700	0.0096
0.031	1 KC	0.7630	0.0095
0.035	1 KC	0.7530	0.0090
0.0025	1 KC	0.8340	0.0080
0.007	1 KC	0.8330	0.0090
0.010	1 KC	0.8200	0.0090
0.015	1 KC	0.8060	0.0090
0.020	1 KC	0.7950	0.0080
0.025	1 KC	0.7840	0.0080
0.031	1 KC	0.7640	0.0090
0.035	1 KC	0.7590	0.0097
0.0015	1 KC	0.8630	0.0094

TABLE V

CALIBRATION DATA FOR DIELECTRIC SAMPLE HOLDER NO. 2 WITH EQUAL - AREA ELECTRODES AND NO SHIELD

Electrode Spacing	Frequency	Capacitance	Dissipation Factor
0.0005"	1 KC	17.5740	0.0020
0.0005"	5 KC	17.5610	0.0055
0.0005"	10 KC	17.5770	0.0100
0.0007"	1 KC	17.5100	0.0020
0.0007"	5 KC	17.4940	0.0055
0.0007"	10 KC	17.5150	0.0100
0.0009"	1 KC	17.4640	0.0020
0.0009"	5 KC	17.4500	0.0055
0.0009"	10 KC	17.4680	0.0100
0.0011"	1 KC	17.4310	0.0020
0.0011"	5 KC	17.4170	0.0055
0.0011"	10 KC	17.4340	0.0100
0.013"	1 KC	17.4040	0.0020
0.013"	5 KC	17.3890	0.0055
0.013"	10 KC	17.4080	0.0100
0.0015"	1 KC	17.3600	0.0020
0.0015"	5 KC	17.3660	0.0055
0.0015"	10 KC	17.3850	0.0100
0.018"	1 KC	17.3570	0.0020
0.018"	5 KC	17.3440	0.0055
0.018"	10 KC	17.3620	0.0100

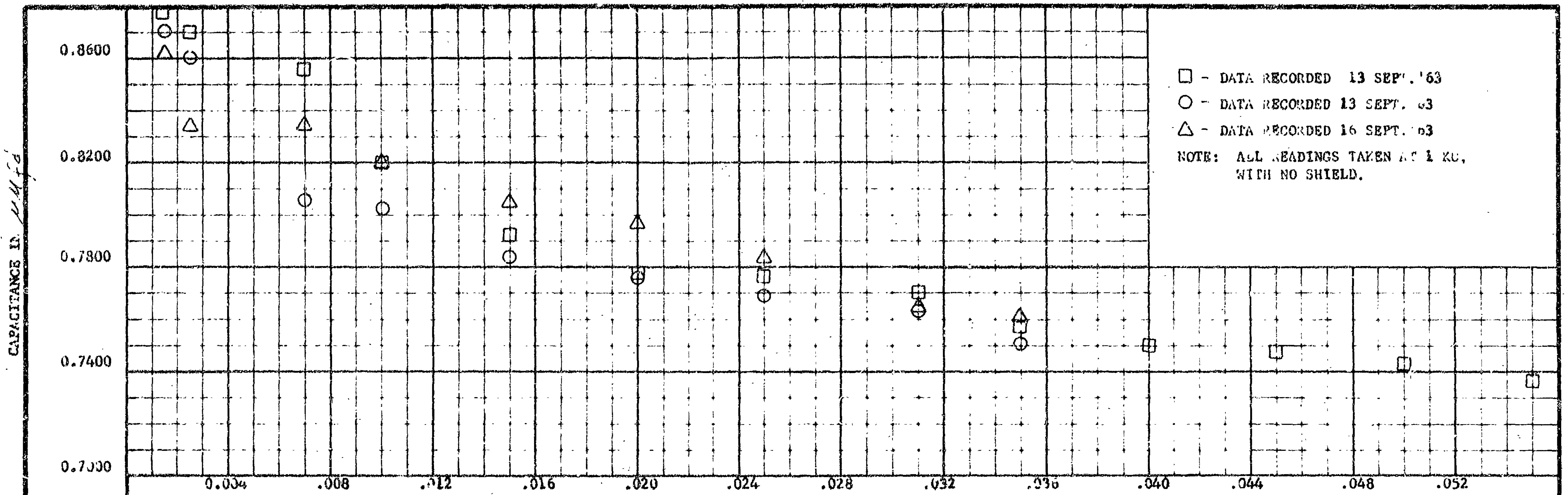


FIGURE 9 CALIBRATION CURVE FOR SAMPLE HOLDER NO. 1 ELECTRODE SPACING, INCHES

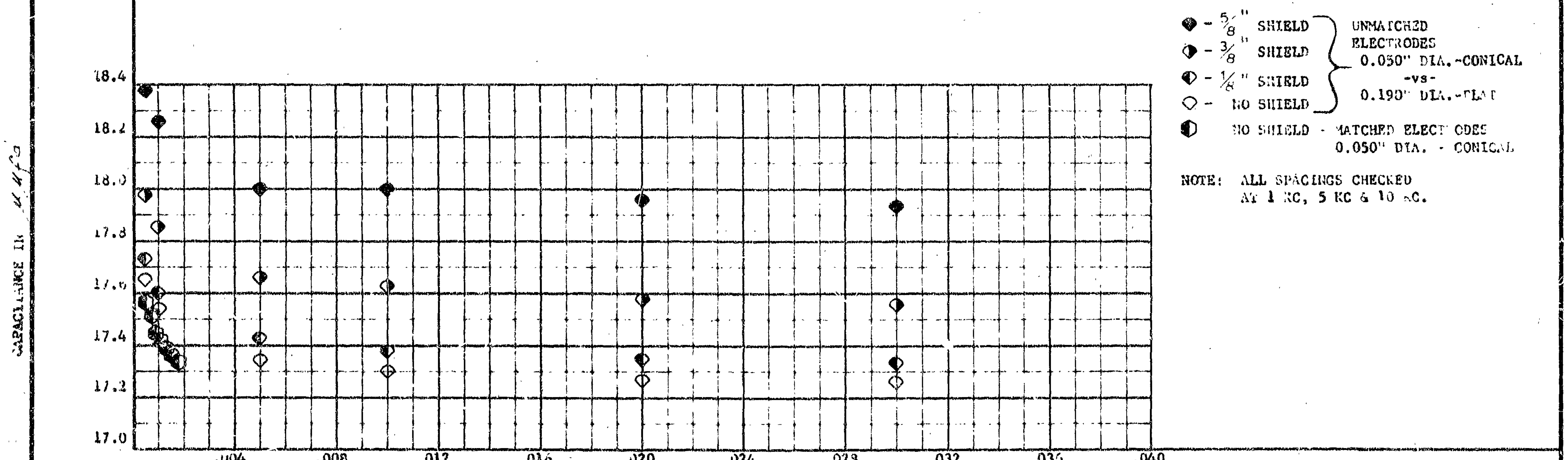


FIGURE 10 CALIBRATION CURVE FOR SAMPLE HOLDER NO. 2 ELECTRODE SPACING, INCHES

paste: the second approach was to use normal Mo-Mn metallizing: the third, and most successful approach was to use metal foil electrodes with vaseline between the specimen and the foil. Results of these tests and dielectric measurement tests are considered in a later section of this report.

b. Optical

The infrared absorption curves were obtained with a Beckman IR-8 spectrophotometer. It is an automatic recording single or double beam instrument designed for the qualitative and quantitative chemical analysis of liquids, solids and gases. Equipped with two gratings and four filters, the IR-8 has a wavelength range from 2.5 to 16 microns. The instrument scans the entire range in 8½ or 25 minutes, recording linearly percent transmittance versus wavelength. Scale expansion, slit program, and time constant are fixed, all parameters having been selected for optimum performance. The double-beam optical system is null balancing, employing an optical attenuator in the reference beam. The single-beam system has a potentiometric null reference which simulates the nulling voltage normally produced by the energy in the reference path, in double-beam operation.

Wavelength reproducibility is .005 from 2.5 to 5 u and .010 from 5 to 16 u. The stray radiation is less than 2%. Frequency accuracy is .008 from 2.5 to 5 u and .015 to 16 u.

For the BeO absorption analysis, double-beam operation was employed. Energy from a Nichrome source is reflected by a pair of parallel mirrors. Thus, two identical beams are emitted from the source, one along the reference path and the other along the sample path. A beam combining section directs reference and sample beams to a chopper mirror rotating at 10 cycles per second. The two beams are alternately directed through the monochromator entrance slit where each beam is collimated on a grating. In the monochromator, each beam is dispersed into its component wavelengths and one narrow band of wavelengths is allowed to pass through the exit slit. Then the beam is focused on a thermocouple where thermal energy is converted into an electrical signal.

Any difference in beam intensity appears in the detector system as an alternating signal having an amplitude proportional to the difference.

The instrument automatically records the linear variation of transmittance as a function of wavelength. Where transmittance is the ratio of radiant energy transmitted to energy incident on sample, both obtained at one wavelength.

The absorption of energy in any spectrum is predicted by Quantum Theory. When the energy of a photon is exactly equal to the differences between two vibrational energy states of a molecule, light will be absorbed. Since the energy of a photon is proportional to the frequency of light, it is seen that the absorption spectrum of a molecule depends upon its natural modes of vibration.

The BeO crystal sample was mounted over a 0.100" hole located in the center of a 2.21" x 2.08" plate and placed in the instrument's sample slot. A similar plate, without the BeO crystal, was placed in the reference slot. Since double-beam operation was used, the plates equalized the beam intensity of both reference and sample. However, by reducing the beam intensity, the amount of thermal energy reaching the detector, was also reduced, thereby weakening the output signal and slowing down the pen response. This problem was easily solved by using plates containing several holes for mounting crystals, allowing more energy to reach the detector.

c. <u>Thermal</u>

A review of the techniques for measurement of thermal conductivity led to the selection of two approaches for making measurements on small BeO single crystals. These techniques are as follows:

(1) <u>Comparative Method</u>

This measurement technique is similar to the so-called cut-bar technique described in ASTM Test Procedure C-408-58 which has been utilized for the measurement of thermal conductivity of ceramic materials. In general, the cut-bar method consists of a series arrangement of a material of known conductivity such as copper with the unknown interposed between two sections of the known material. Thermocouples placed at predetermined spacings in both the known and the unknown allow calculation of Q (heat flow) once a thermal gradient is established, and K may be calculated based on the ΔT along the sample. In general, this technique is carried out in vacuum and is a relatively simple method. The only complications that arise are usually in the attachment of the sample to the known material. In the measurement of single crystal beryllium oxide the size and geometry of known specimen material is extremely small and therefore for these tests it has been decided to utilize the fiber or whisker type of single crystal which will provide data in one crystallographic direction. The apparatus consists basically of an electrical heat source, a differential thermocouple probe which acts as the known standard on the hot side and to which the tip of the crystal is attached. The heat sink is a liquid low melting alloy material into which the cold tip of the crystal may be immersed so as to establish the thermal gradient. The entire apparatus is designed to be operated in vacuum and should provide data at temperatures up to approximately 200°C above which radiation losses could become an error source. Figures 11 and 12 show the apparatus and active components used in this method.

(2) The Dynamic Method

Arrangements were made with Queens Laboratory of Edison, New Jersey to develop a dynamic or pulse technique for the measurement of the thermal conductivity of the platelet form of BeO single crystal.

Through the efforts of Dr. H. T. Smyth and Dr. W. Bauer, the physical calculations were made, and preliminary experiments run to evaluate this method as a means of measuring thermal conductivity. A small sub-contract was initiated to cover the initial stages of this work and was sufficient to establish the feasibility of the method. It basically consists of the introduction of a chopped light source onto one side of the crystal, each side of the platelet having a vapor deposited bi-metallic film thermocouple. Based on the frequency of the heat energy and the temperature gradient established across the crystal the thermal conductivity may be calculated. Initial tests conducted with glass microscope slides and polycrystalline BeO simulated crystals established the applicability of such a technique to the measurement of monocrystalline BeO properties. Appendix 1 contains a complete description of the technique, and full discussion of the results gained.

(c) Results

1. Task A - Single Crystal Growth

The nucleation and growth of pure, single crystals of BeO has been accomplished in two completely different environments. The quality of single crystalline product has been very good, but considerable work is still necessary to advance the state-of-the-art to a position where crystal size is significantly increased. The most success has been achieved with the water-vapor transport method; while results of the crystallization experiments indicate a very strong potential for this process.

a. Water-Vapor Transport Method

The experiments performed under this phase of the program are listed in Table I. Crystals grown by this technique have been hexagonal in cross-section with diameters of 0.050 - 0.060" and many crystals up to 0.175" diameter. Chemical purity of these crystals is better than 99.9%. Surface impurities constitute nearly all of the contamination. The main sources of contamination are in the incoming carrier gas containing reactive steam, and in the nutrient BeO materials.

Several experiments were run where the seed plates were pretreated with hydrofluoric and hydrofluorosilicic acids. In these experiments, crystal nucleation was greater in the regions treated with hydrofluoric acid, and less in regions treated with hydrofluorosilicic acid. This difference is believed to be due to the leaching out of impurities from the surface of the seed plate, and can be considered similar to the different nucleation/growth potentials at the surface of growing and contaminated crystals. This similarity and knowledge of the role of impurities in the flux growth method and in the evaporation-condensation process point up quite strongly the need for observing the controls set forth below and especially those pertaining to the purity of the system.

(1) The reaction zone is constructed completely of pure polycrystalline beryllium oxide to minimize impurities present in the system.

(2) Nutrient material utilized as a source for beryllium hydroxide is high purity sintered beryllium oxide grit or scraps and the seed material is also beryllium oxide.

(3) Induction heating through the use of the graphite susceptor system is initiated with very rapid heating rated on the order of 7°C per minute.

(4) Water vapor is introduced at a temperature of 1200°C into the reaction zone using helium as a carrier gas.

(5) Water flow rates are on the order of 2 cc per minute.

(6) Vaporizer bath temperature should be 180°C.

(7) The high temperature reaction zone where evaporation of the beryllia occurs is between 1775 and 1825°C.

(8) A reaction holding time of 2½ hours is utilized.

The close control of seed surface conditions so as to yield platelets in the proper section of the reaction chamber, the reaction chamber temperature, and the vaporizer temperature as it controls the water content of the carrier gas, are three parameters which need much better control in order to yield

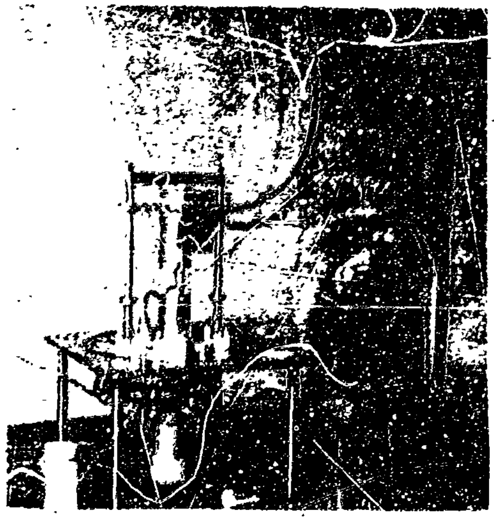


FIGURE 11

Low Temperature Fiber Thermal Conductivity Apparatus

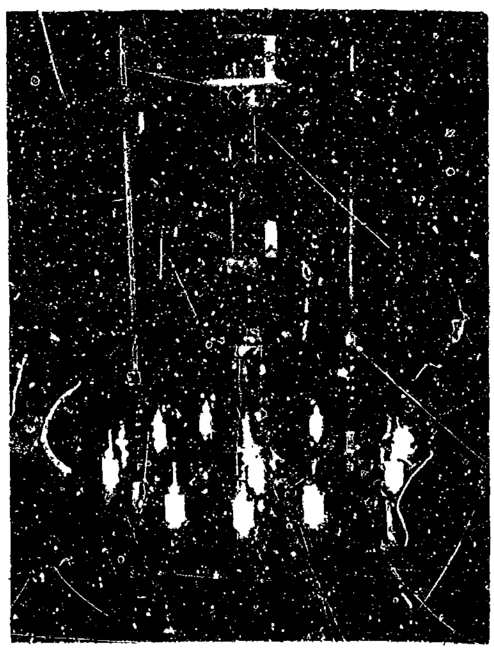


FIGURE 12

Active Components for Fiber Thermal Conductivity Apparatus high purity single crystals of BeO large enough to be useful in prototype fabrication and testing. Variations of as little as ± 5°C in the vaporizer bath temperature have been found to modify crystal habit from either a fibrous or cotton-like condensate to the platelet form which is desired.

b. Solution Growth Experiments

Preliminary experimental runs were made with the platinum-wound furnace. At temperatures in the vicinity of 1375°C a reaction occurred between the platinum winding and the Al_2O_3 muffle. After several attempts to make use of the platinum-wound furnace, it became evident that the present system was not compatible with the MoO_3 vapors above the solution. A second solution growth furnace was constructed using Globar heating elements in an Al_2O_3 muffle. The furnace was calibrated in the temperature range 1300 - 1500°C, and several solubility experiments were run to determine the best operating conditions and growth parameters. Table II lists these experimental runs and their results. Use has been made of both Li_2MoO_4 and $Li_2Mo_2O_7$ with MoO_3 and spherical BeO powder (-325 mesh). Results to date indicate that Li_2MoO_4 with excess MoO_3 is better than $Li_2Mo_2O_7$ with excess MoO_3. It is also indicated that the Li_2MoO_4 made from LiOH and MoO_3 was better than the commercially available Li_2MoO_4, the reason probably being associated with the 17.2% excess Li_2O present in the commercially available material.

Data indicate that at 1455°C approximately 0.25 mole of BeO may be dissolved in Li_2MoO_4:1.25 MoO_3. Crystallization of BeO microcrystals was accomplished at 1425°C after a mixture of Li_2MoO_4, MoO_3 and BeO (Molar ratio 1:1.25:0.5, respectively) was heated to 1455°C for a period of 30 hours then held at 1425°C for 48 hours. These crystals were no more than 0.005 - 0.010" in cross section but displayed many of the physical characteristics associated with crystals grown from alkali molybdate solutions by other investigators.

These identifying characteristics include complete transparency, hexagonal cross-section, and hemi-pyramidal growths from the basal surface. (Fig.13) Growth rates have been reported in the vicinity of 0.001" per day. Growth rates with Li_2MoO_4 made up by National Beryllia appear to be somewhat faster and continued efforts will be directed toward perfection of the process to produce larger crystals faster.

For better control and faster growth, an artificial temperature gradient has been built into the system using BeO heat sink blocks and BeO rod (1/4" x 1" x 3¼") between the heat sink and the platinum reaction crucible. With this set of conditions it is possible to maintain a temperature of 1455°C on the platinum crucible and 1325°C on the heat sink end of the heat transfer

FIGURE 13
PHOTOMICROGRAPHS OF MICROCRYSTALS
FROM SOLUTION GROWTH EXPERIMENTS

rod. One additional heat transfer rod has been introduced between the melt and the heat sink to complete the necessary artificial gradient. This design offers the possibility of securing a definite and controllable thermal extraction area.

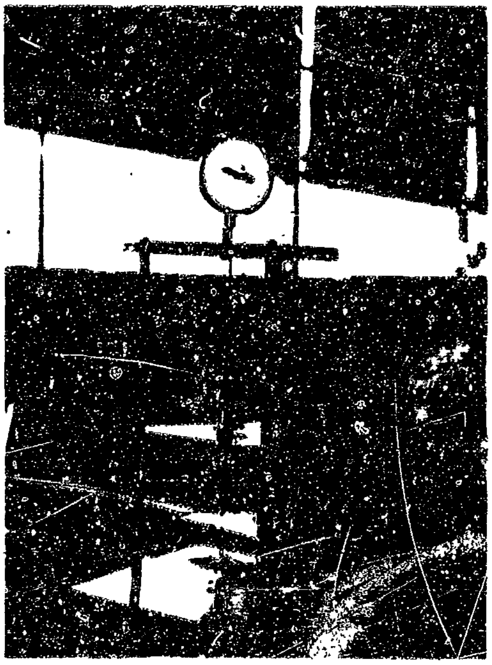
2. Task B - Properties Determinations

a. Dielectric Properties

Figures 7 and 8 show a plot of capacitance as a function of distance between electrodes for sample holders 1 and 2. These data were used in calibration of the sample holders with and without concentric metal shields. It was found that metal shields were not necessary and, in fact, led to misinterpretation of data. The small diameter of the shield introduced error into the system through the added high lead-to-shield capacitance. Data gained on both sample holders without a shield was more reliable, realistic and reproducible. In the case of the sample holder No. 2, the design of the holder itself affords sufficient shielding except in a case where a fluorescent loop light is operated very close to the test apparatus. In this case the 60 cycle pickup by the bridge assembly appears to have a greater effect on the readings than sample interference. Capacitance readings shown in Tables IV and V are representative of the capacitance of the complete holder, which should remain constant and the varying capacitance of the air gap. The composite capacitance is shown as a function of the electrode spacing. The difference in sample holder unit capacitance accounts for the difference in capacitance readings for the two holders with the same electrode spacing. One additional alteration was necessary to improve the quality of the readings. This involved the reworking of the ground electrode to produce two equal diameter electrode probes, and prevented the inclusion of stray capacitance readings around the edges of the BeO crystals (Figures 14 and 15).

Preliminary calibration of the unit using sample specimens of polycrystalline BeO between 0.092" and 0.012" thick was completed prior to initiating tests on single crystals. Data gained from this calibration - standardization portion of the program pointed up several important facts useful in later testing of single crystals.

Dielectric measurements on single crystal platelets of BeO were first made using two electrodes of different cross-sectional areas. The high lead was 0.050" diameter with a low angle taper: the ground electrode was a pedestal of uniform 0.190" diameter. The single crystal samples were positioned between



FIGURE

PHOTO OF SAMPLE HOLDER NO. 2

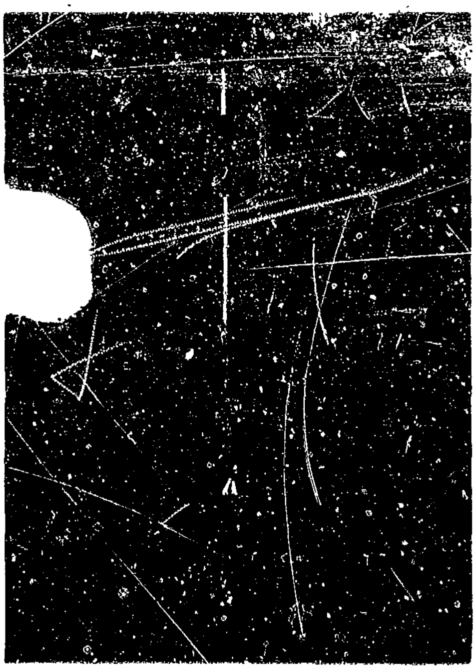


FIGURE 15

PHOTO OF ELECTRODE ASSEMBLY OF SAMPLE HOLDER NO. 2

the unit electrodes with silver paste squeezed into surface-conforming electrodes in contact with both faces of the crystal. Capacitance readings were taken and the electrode areas were measured. Several faults were found with this type of set-up.

(1) Measurements of exact areas of contact were very poor due to size and irregularity of shapes of crystals.

(2) Silver pastes (and other pastes) do not constitute pure metallic electrodes and the contaminants present contribute to the total capacitance of the system.

(3) As the thickness of the silver paste electrodes varied the high lead-to-ground stray capacitance varied and was not measurable.

(4) Handling of crystals and application of pressure were very difficult and in many cases resulted in damage to the crystal.

Following alterations in unit electrode design, the following procedure was used in measuring dielectric properties of single BeO platelets.

(a) Specimen was selected with hexagonal cross-section and surface free of spurious growths and other imperfections.

(b) Two tin foil electrodes of 0.050" diameter cross-section were fabricated between high lead and ground electrodes of equal cross-section.

(c) Surfaces of tin foil electrodes were treated with vaseline, and electrodes were positioned on unit electrode tips.

(d) Single crystal platelet was positioned on foil on ground electrode and high lead electrode was brought in contact using micrometer advance.

(e) Capacitance measurements were made with several different electrode contact pressures.

(f) Singlo crystal specimen was removed to metallograph for exact measurement of thickness.

Table VI lists dielectric test data for single crystal BeO platelets. All measurements were made parallel to the c-axis.

TABLE VI

DIELECTRIC TEST DATA FOR SINGLE CRYSTAL BeO - ALL MEASUREMENTS MADE PARALLEL TO C-AXIS

IDENTITY	THICKNESS	A/t	Cv	Cx	FREQUENCY	DIELECTRIC CONSTANT	DISSIPATION FACTOR
CP II 2	0.001"	1.965	0.441	2.4000	1 KC	5.45	0.0001
				2.3190	10 KC	5.28	0.0001
				2.6840	1 KC	6.09	0.0001
				2.6310	5 KC	5.98	0.0001
				2.6790	10 KC	6.09	0.0001
CP II 14	0.0018"	1.09	0.2449	1.2220	1 KC	5.0	0.0001
				1.2770	5 KC	5.25	0.0001
				1.2970	10 KC	5.32	0.0001
				1.2910	1 KC	5.29	0.0001
				1.3290	5 KC	5.44	0.0001
				1.3440	10 KC	5.51	0.0001
CP II 15 Thinner Section	0.0012"	1.64	0.367	1.6745	1 KC	4.56	>0.0001
				1.6920	5 KC	4.61	>0.0001
				1.6990	10 KC	4.64	>0.0001
CP II 15 Thicker Section	0.0018"	1.09	0.2449	1.6745	1 KC	6.88	0.0001
				1.6920	5 KC	6.91	0.0001
				1.6990	10 KC	6.96	0.0001
CP II 2 Re-runs	0.0014"	1.40	0.314	2,400	1 KC	7.65	0.0001
				2.319	10 KC	.38	0.0001
				2.684	1 KC	8.55	0.0005
				2.631	5 KC	8.37	0.0001
				2.679	10 KC	8.52	0.0001

TABLE VI (con't)

DIELECTRIC TEST DATA FOR SINGLE CRYSTAL BeO - ALL MEASUREMENTS MADE PARALLEL TO C-AXIS

IDENTITY	THICKNESS	A/t	Cv	Cx	FREQUENCY	DIELECTRIC CONSTANT	DISSIPATION FACTOR
CP II 17	0.001"	1.965	0.441	2.5996	1 KC	5.895	0.00001
Light				2.5974	5 KC	5.89	0.001
Contact				2.5940	10 KC	5.88	0.002
CP II 17	0.001"	1.965	0.441	3.1230	1 KC	7.082	0.0002
Very tight				3.1185	5 KC	7.07	0.0001
Contact				3.1190	10 KC	7.07	0.002
CP II 19	0.0013"	1.515	0.339	1.9860	1 KC	5.86	0.00001
				1.8870	5 KC	5.566	0.00001
				1.8920	10 KC	5.581	0.00001

TABLE VII

RESISTIVITY DATA FOR SINGLE CRYSTAL BERYLLIA

IDENTITY	THICKNESS	A/t	TEST CONDITIONS	READING	VOLUME RESISTIVITY
CP II 2	0.00356 cm	3.56	Not dried 1000 wvdc	60×10^{12} ohms	2.13×10^{14} ohm-cm
CP II 1	0.00254	5.0	Not dried 1000 wvdc	$15\text{-}50 \times 10^{12}$ ohms	2.5×10^{14} ohm-cm
CP II 9	0.00304	4.16	Not dried 1000 wvdc	45×10^{12} ohms	1.87×10^{14} ohm-cm
CP II 9	0.00304	4.16	Dried 85°C/20 min. 1000 wvdc	$50 \times 10^{13} - \infty$ ohms	2.08×10^{15} ohm-cm
CP II 9	0.00304	4.16	Dried 125°C/4 hrs. 1000 wvdc	∞	10^{16} ohm-cm
CP II 7	0.00356	3.56	Dried 85°C/20 min. 1000 wvdc	∞	10^{16} ohm-cm
CP II 1	0.00254	5.0	Dried 125°C/4 hrs. 1000 wvdc	50×10^{13} ohms	2.5×10^{15} ohm-cm
CP II 15	0.00457	2.77	Dried 125°C/4 hrs. 1000 wvdc	50×10^{13} ohms	1.39×10^{15} ohm-cm

Polycrystalline BeO has a dielectric constant of 6.3. Sample holder No. 2 was calibrated and standardized with thin wafers of polycrystalline BeO produced by cold-pressing and sintering, and by hot-pressing techniques.

It is interesting to note that on crystal CP II-17 a dielectric constant of 5.89 was established by holding the crystal lightly; however, when the electrodes were tightened on the crystal, a dielectric constant of 7.07 was established. This crystal showed the least number of surface imperfections of the crystals tested. This same characteristic response to pressure was also evidenced with several other crystals, indicating that as pressure was increased the interface vaseline was squeezed out and the readings more closely described the true capacitive nature of the single crystal BeO. A discussion of these results and the anisotropic characteristics of single crystal platelets of BeO is contained in a later section of this report.

Table VII lists data on the volume resistivity of single crystals of BeO measured parallel to the c-axis. The instrument used was a Type H Teraohmmeter capable of measurements to 500 teraohms at 1000 wvdc. All measurements were made after at least one (1) minute at a given working voltage, and after a stable temperature had been established for at least five (5) minutes. Room temperature tests were conducted at 200, 400, 600, 800 and 1000 wvdc levels. Elevated temperature tests were conducted at 200 and 500 wvdc levels to temperatures of 125°C. Results indicate that the volume resistivity at room temperature and 500 wvdc is higher than can be accurately measured with a teraohmmeter, and appears to be at 10^{15} ohm-cm to 10^{18} ohm-cm. It is definitely well in excess of 500 teraohms at room temperature and up to 1000 wvdc applied parallel to the c-axis for extended periods of time.

b. Optical Properties

A study was made of the optical characteristics of beryllia single crystals in the infrared range which will relate directly to the ability of the crystals to transmit heat when utilized in conjunction with various component devices. The spectrum studied was from 2.5 to 16 microns. The technique was similar to that used for material which could be formed into a continuous film. The infrared test data is shown in graphical form in Figures 16 and 17. Analysis shows 99% transmission from 2.5 to 7 microns for single crystals, above which it exhibits strong absorption. Transmission decreases to 8% at 8 microns where it remains constant to 16 microns. For comparison purposes corresponding data was obtained on mosaic structures made up of several single crystals, 95% dense cold pressed and sintered BeO and theoretically dense hot-pressed BeO of 99% purity. Transmission characteristics for mosaic structures were similar to single crystals, but transmission level was lower due to fixturing and misorientation. A noticeable absorption peak occurs in the BeO single crystal at about 7.3 microns and a mino peak occurs at 6.5 microns. These absorption peaks were reproducible over several BeO monocrystalline samples mounted in various ways with both slow and fast scan on the spectrophotometer indicating a fundamental behavior of the crystal structure.

c. Thermal Properties

Considerable work was done under this portion of the program to establish the feasibility of using a method defined as unsteady state heat flow through thin sheets. (4) This work was conducted at Queens Laboratory, Edison, New Jersey. A full report was submitted to National Beryllia by Queens Laboratory and is included in Appendix 1 to this report.

IV. SUMMARY AND CONCLUSIONS

Task A. Single Crystal Growth

The growth of single crystals of beryllium oxide by the water vapor transport method has been the most successful method of preparing single crystals in a form useful for determining the anisotropic characteristics of their physical properties. The continued growth of small platelets to yield larger, more useful test samples is mainly dependent upon the thermodynamic properties of the system and the impurities present in the system as they affect the nucleation and kinetics of growth. Growth by crystallization from solution shows very definite possibility as an alternate method to produce monocrystalline beryllium oxide if the crystallization-growth controlling parameters may be better defined and controlled.

Task B. Dielectric, Optical and Thermal Properties

Several investigators (5) have reported the crystal structure of beryllium oxide to be a dihexagonal structure. Piezoelectric characteristics have been identified and are similar to what one would expect based on the crystal structure and hemi-pyramidal crystal characteristics and the physical response to chemical etching.

Predictions on the anisotropic dielectric properties of BeO follow two general trains of thought. One line of thought would expect deviation of the dielectric constant for single crystal material from the average value for polycrystalline material based on the relative inter-atomic distances in the "c" and "a" directions. Cell constants have been determined by x-ray analysis as $a_o = 2.6979 \pm 0.0002$ Å, and $c_o = 4.3772 \pm 0.0002$ Å, c/a = 1.63. Another line of thought would expect deviation based upon the relative interplaner distances and the bond distances. In this case the Be-O bond distance parallel to the c-axis is 1.659 Å, and the Be-O bond distance at $108^\circ 47'$ from the c-axis is 1.645 Å.

If one considers only the cell constants (c/a ratio of 1.63) he could expect that the dielectric constant in the "c" direction should be less than 6.3, and in the "a" direction more than 6.3.

Using the same inter-electron effectiveness reasoning, but considering the interplanar as well as the inter-atomic distances between dissimilar atoms one could expect that the dielectric constant in the "c" direction should be more than 6.3, and in the "a" direction should be less than 6.3. Interplanar distances are 1.659 Å, and 0.5297 Å; inter-atomic distance between dissimilar atoms on a planar projection is 1.5574 Å.

It is interesting to note that on crystal CP II 17 a dielectric constant of 5.89 was established by holding the crystal lightly; however, when the electrodes were tightened on the crystal, a dielectric constant of 7.07 was established. This crystal showed the least number of surface imperfections of the crystals tested. This same characteristic response to pressure was noticed on several crystals, indicating that as the pressure was increased, the interface vaseline was squeezed out and the readings more closely described the true capacitive nature of the single crystal BeO.

In measuring the volume resistivity of single crystals of beryllium oxide it was difficult to properly evaluate the electrical characteristics due to the size and shape of the platelets. However, it is quite evident that the volume resistivity of monocrystalline platelets of BeO tested with 1000 wvdc applied parallel to the "c" crystallographic direction is well in excess of 10^{15} to 10^{18} ohm-cm at temperatures up to 125°C.

Infrared transmission-absorption characteristics were determined in the range from 2 to 16 microns. It was established that single crystals of BeO exhibit nearly 99% transmission in the range 2 to 7 microns, with a major absorption peak at 7.3 microns and a minor absorption peak at 6.5 microns. Transmission decreases to approximately 8% at 8 microns and remains constant through 16 microns. Cold-pressed and sintered BeO with density of 95% showed almost total absorption throughout the 2 to 16 micron range. Theoretically dense hot-pressed BeO of 99% purity showed optical characteristics similar to those of single crystal BeO in the positions of the absorption peaks, but different in the transmission and absorption levels. Mosaic structures made up of several crystals of BeO showed similar characteristics to single crystals but lower transmission level due to fixturing.

Tests run by Queens Laboratory for National Beryllia Corp. on the determination of anisotropic thermal properties of monocrystalline BeO by the unsteady state heat flow method showed the method would be acceptable for measuring the thermal conductivity of single crystal platelets of BeO. No tests were run on BeO single crystals.

When reviewing the above summary of data, accumulated during the course of this investigation, it becomes evident that there exists a very definite need for further studies of the anisotropic characteristics of monocrystalline BeO. Results gained under the present contract are in good agreement with those gained through several other investigators. However, not enough conclusive data has been generated which can fully describe the anisotropic characteristics of BeO. A sufficient basis, both in experience and in results, has been established to assure a rapid coordination of facts into a truly conclusive description of these anisotropic characteristics through continued studies.

Figure 16 - BERYLLIUM OXIDE SINGLE CRYSTAL INFRARED TRANSMISSION

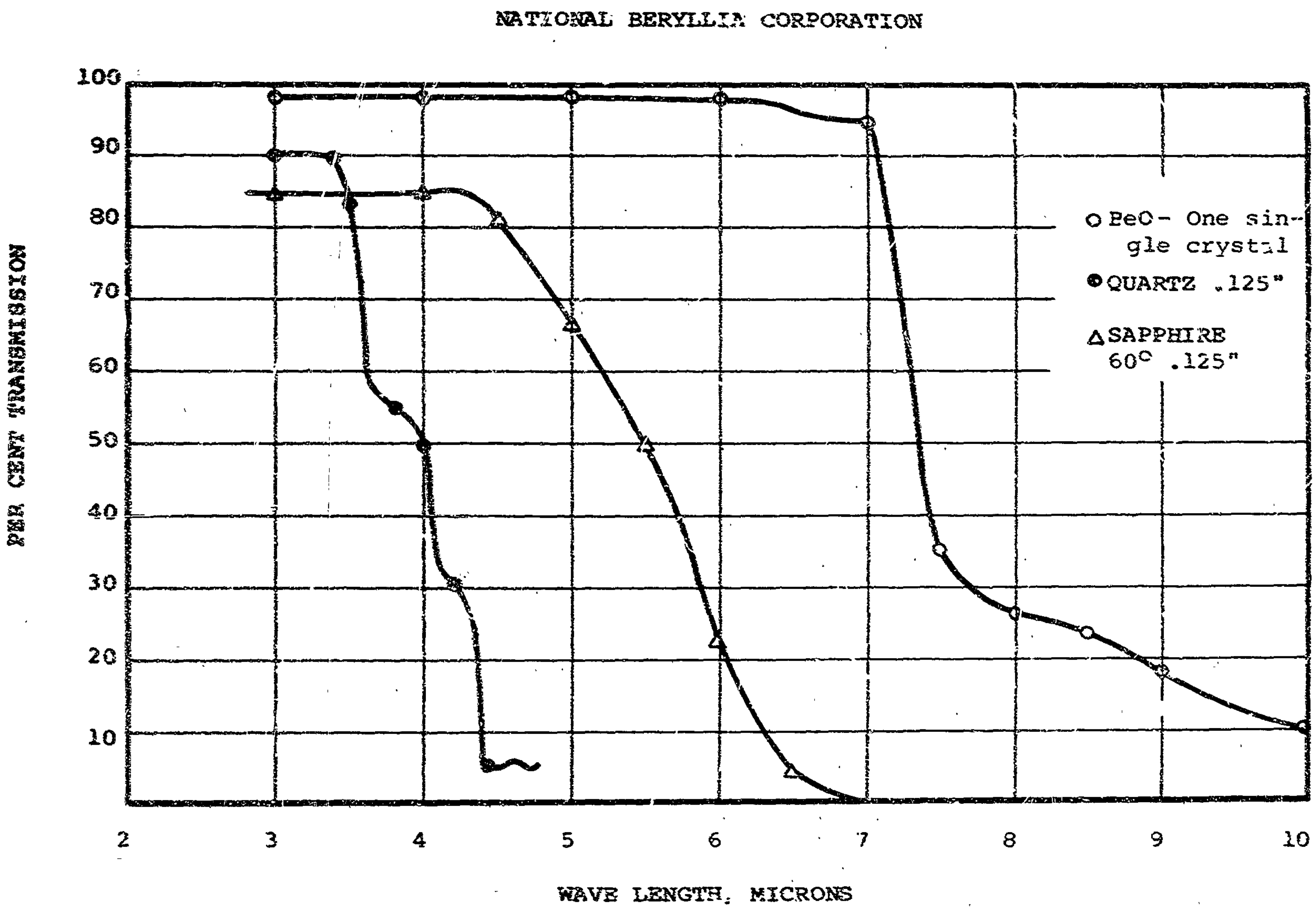
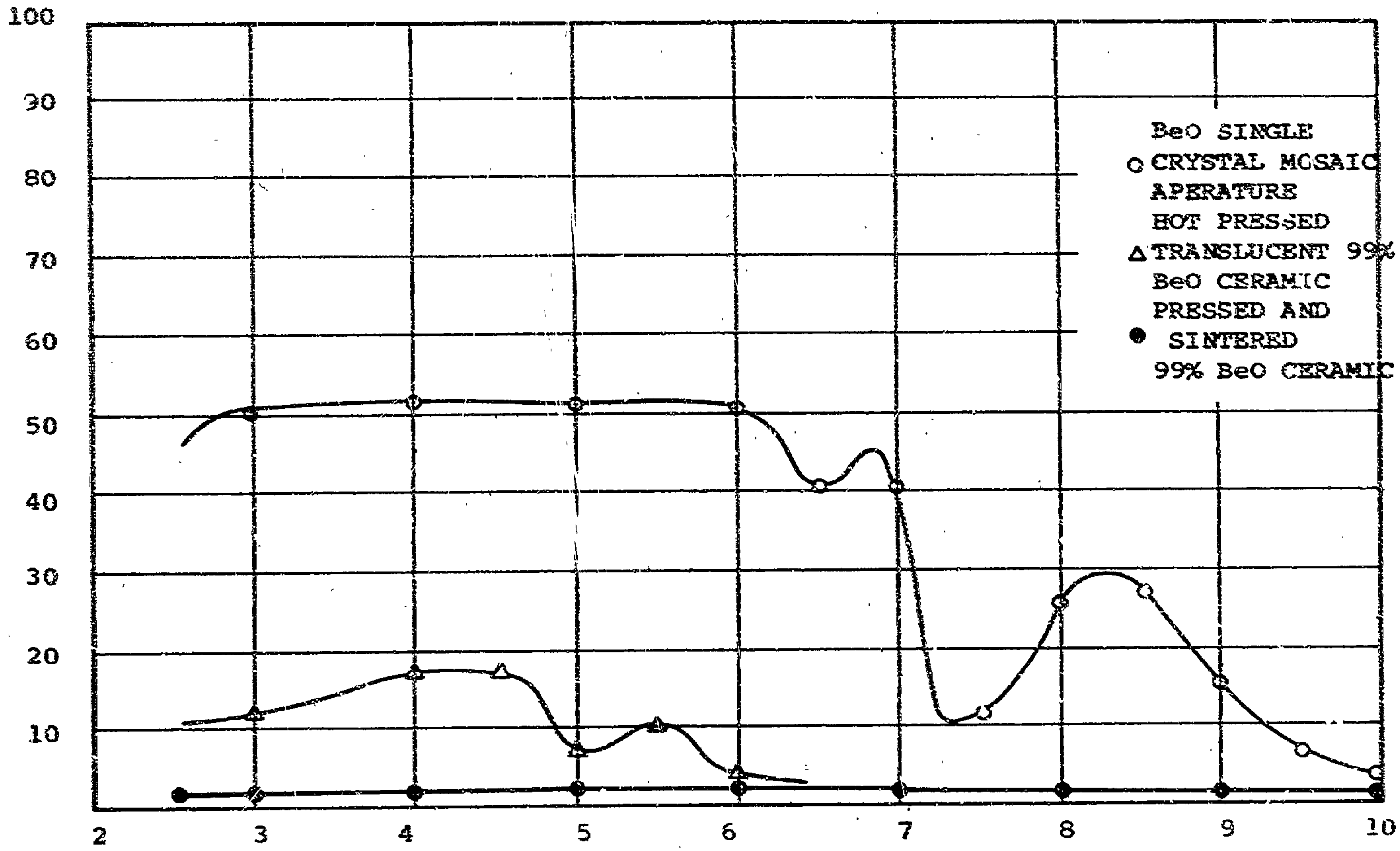


FIGURE 17

INFRA-RED TRANSMISSION OF BeO CRYSTAL MOSAIC APERTURE



REFERENCES

1. "High-Temperature Resistant Beryllia Fiber-Reinforced Structural Composites", Technical Documentary Report No. ASD-TDR-62-632 July 1962, Directorate of Materials and Processes, Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Project No. 7340, Task No. 734003, Prepared under Contract No. AF 33(616)-8066 by the National Beryllia Corporation, Haskell, New Jersey.

2. "Beryllia Oxide Single Crystal Growth - 1. Alkali Molybdate Method", by S. B. Austerman, A. R. Hopkins, Atomics International A Division of North American Aviation, Inc., P. O. Box 309, Canoga Park, California, Contract AT(11-1)-GEN-8.

3. "Growth of Beryllium Oxide Single Crystals", Herbert W. Newkirk and Donald D. Kingman, California University, Livermore. Lawrence Radiation Laboratory, 1962, Contract W-7405-eng-48.

4. Parker, W. J., Et. Al., "Flash Method of Determining Thermal Diffusivity, Heat Capacity and Thermal Conductivity", Journal Applied Physics 32 (9) (1679) 1961.

5. Smith, D. K., Newkirk, H. W., Kahn, J. S., Lawrence Radiation Laboratory (Livermore) Rpt. W-7405-eng.-48, 4 October 1962.

STUDY OF IMPROVED BERYLLIUM OXIDE MATERIALS FOR MICROELECTRONICS TECHNOLOGY

Appendix A
to
Final Report for the Period
8 April - 8 December, 1963
Contract NASw-685

Unsteady State Heat Flow Through Thin Sheets

Prepared for
National Beryllia Corporation
Haskell, New Jersey

by
Queens Laboratory Incorporated
Edison, New Jersey

H. T. Smyth
J. F. Mooney

UNSTEADY STATE HEAT FLOW THROUGH THIN SHEETS

Introduction

Outlined below is the preliminary investigation of the feasibility of measuring thermal diffusivity of ceramic materials by studying the flow of a sinusoidal temperature variation through a thin sheet of the material. The problem is over-simplified and in practice there will be the obvious necessity of handling various corrections, or designing the experiment so as to minimize the necessity for those corrections. The corrections will be mentioned at the end but not studied in detail at this stage of the investigation.

Idealized Conditions

The sample, in the form of an infinite sheet of finite thickness, is subjected on one side to a heat flux which varies sinusoidally with time so that in one half cycle it is receiving and in the other half cycle it is emitting. The surface of the sheet is considered opaque to whatever radiation is falling on it, and all radiation emitted is considered to be radiated from the surface, not the interior. The other surface is considered to be perfectly insulated so that there is no heat flow into or out of this surface. Radiation transfer within the sheet is also neglected.

The flow of heat to the irradiated side will be taken to have the form

$$I_0 \sin \omega t \qquad \text{cals/cm}^2\text{/sec}$$

The boundary condition will be

$$I_0 \sin \omega t = -k \frac{\partial T}{\partial x}$$

where k is the thermal conductivity. This heat will pass into the interior in the form of a decaying temperature wave of the form

$$A e^{-\sqrt{\frac{\omega}{2\alpha}}x} \cos\left(\omega t - \sqrt{\frac{\omega}{2\alpha}}\, x\right) + B e^{-\sqrt{\frac{\omega}{2\alpha}}x} \sin\left(\omega t - \sqrt{\frac{\omega}{2\alpha}}\, x\right)$$

where α is the thermal diffusivity of the material and A and B are arbitrary constants to be determined so that the boundary condition is satisfied.

The front wall (receiving the radiation) is taken to be located at $x = 0$ and the insulated backwall at $x = a$. The incoming thermal wave will generate a reflected wave at the backwall of such a form that the addition of the incoming and reflected waves gives a zero gradient at $x = 0$. The wave will be again reflected at $x = 0$ the two waves adding up to give zero gradient so that the first boundary condition is still satisfied. The wave can be followed until it has decayed to where it has no significant effect on the temperature variation.

To satisfy the first boundary condition at $x = 0$ $\left(I_0 \sin \omega t = -k \frac{\partial T}{\partial x}\right)$ it comes out that

$$B = \frac{I_0}{\sqrt{2\omega k \rho c}}$$

$$A = -\frac{I_0}{\sqrt{2\omega k \rho c}}$$

It turns out that the absolute magnitude and the phase of the first thermal wave going into the sheet are not important since the method ultimately reduces to measurement of the ratio of amplitude variation on the two faces.

The incoming temperature wave is written thus in the form

$$T = C e^{-\sqrt{\frac{\omega}{2\alpha}}\,x} \cos\left\{\omega t - \sqrt{\frac{\omega}{2\alpha}}\,x\right\}$$

The first reflected wave (at $x=a$) is written

$$T = C e^{-\sqrt{\frac{\omega}{2\alpha}}(2a-x)} \cos\left\{\omega t - \sqrt{\frac{\omega}{2\alpha}}(2a-x)\right\}$$

The next reflected wave (at $x=0$) is written

$$T = C e^{-\sqrt{\frac{\omega}{2\alpha}}(2a+x)} \cos\left\{\omega t - \sqrt{\frac{\omega}{2\alpha}}(2a+x)\right\}$$

The next (at $x=a$) is

$$T = C e^{-\sqrt{\frac{\omega}{2\alpha}}(4a-x)} \cos\left\{\omega t - \sqrt{\frac{\omega}{2\alpha}}(4a-x)\right. \qquad \text{etc.}$$

These represent the waves traveling back and forth until their amplitude becomes negligible.

The temperature at $x=0$ is given by

$$T = C\cos\omega t$$
$$+\ 2Ce^{-\sqrt{\frac{\omega}{2\alpha}}\,2a}\left\{\cos\omega t\cos\sqrt{\tfrac{\omega}{2\alpha}}\,2a + \sin\omega t\sin\sqrt{\tfrac{\omega}{2\alpha}}\,2a\right\}$$
$$+\ 2Ce^{-\sqrt{\frac{\omega}{2\alpha}}\,4a}\left\{\cos\omega t\cos\sqrt{\tfrac{\omega}{2\alpha}}\,4a + \sin\omega t\sin\sqrt{\tfrac{\omega}{2\alpha}}\,4a\right\}$$
$$\text{etc.}$$

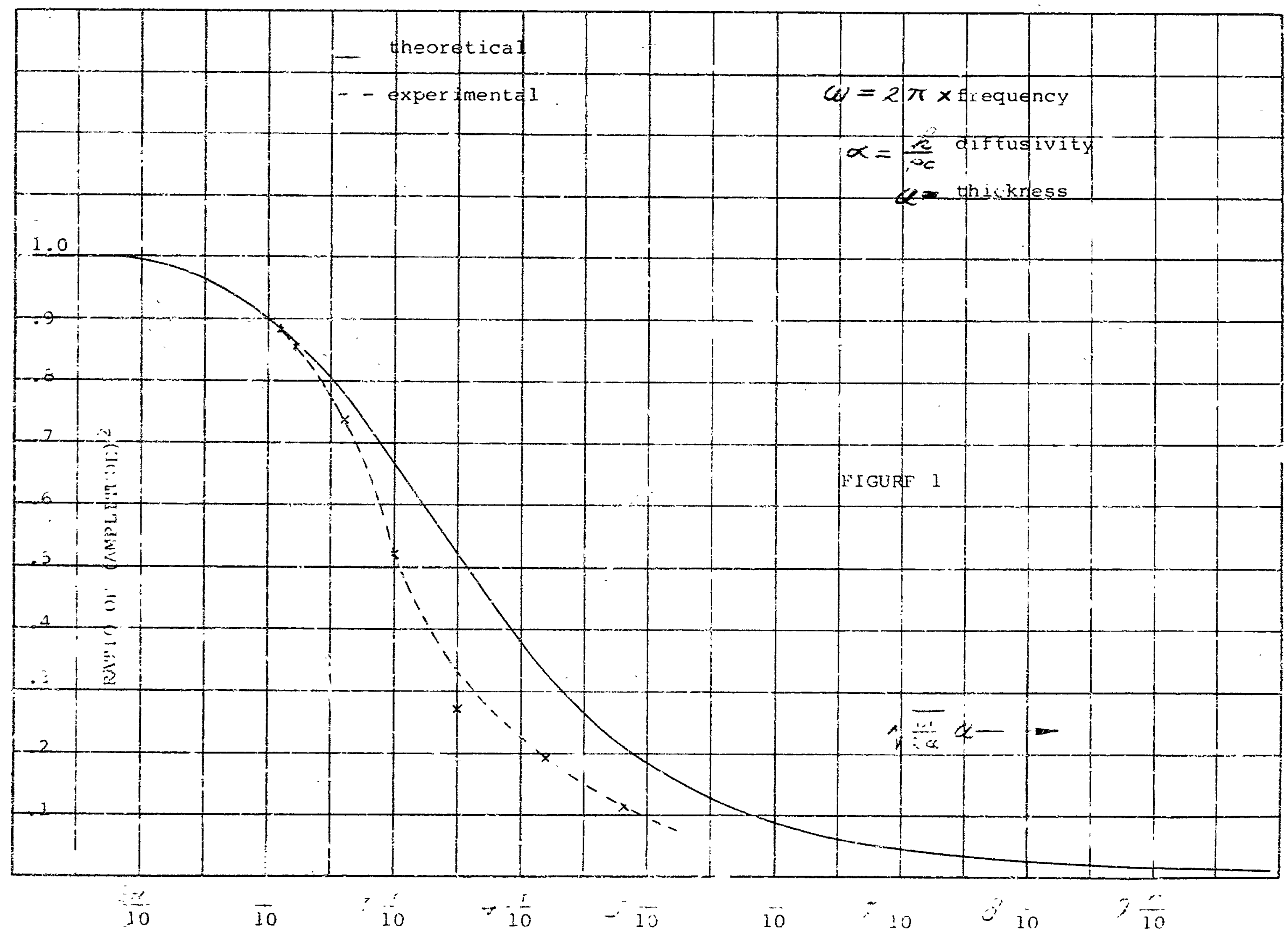
and at $x = a$ the temperature is given by

$$T = 2Ce^{-\sqrt{\frac{\omega}{2\alpha}}\,a}\left\{\cos\omega t\cos\sqrt{\tfrac{\omega}{2\alpha}}\,a + \sin\omega t\sin\sqrt{\tfrac{\omega}{2\alpha}}\,a\right\}$$
$$+\ 2Ce^{-\sqrt{\frac{\omega}{2\alpha}}\,3a}\left\{\cos\omega t\cos\sqrt{\tfrac{\omega}{2\alpha}}\,3a + \sin\omega t\sin\sqrt{\tfrac{\omega}{2\alpha}}\,3a\right\}$$
$$+\ \text{etc}$$

For values of $\sqrt{\frac{\omega}{2\alpha}}\,a$ ranging from 0 to π in steps of $\frac{\pi}{10}$ these two expressions were summed and amplitudes were computed by taking the square root of the sums of the squares of the coefficients of sin ωt and cos ωt after the summation had been carried out. The resulting curve is plotted in Fig. 1 with the ordinate expressed as the ratio of the square of the amplitudes of the temperature variation on the two faces of the sheet.

Experimental Arrangement

After some preliminary tests the following arrangement was set up to make a quick check of the experimental feasibility. The sample was a single crystal of magnesium oxide of thickness .025 cms. The surface temperatures were read by depositing on the surface by sputtering a thin coat of platinum. In order to get a sufficiently high resistance the electrical path was a maze made by masking during the sputtering. An approximate design is shown in Fig. 2.



theoretical
- - experimental
ω = 2π x frequency
α = k/ρc diffusivity
a = thickness
FIGURF 1
RATIO OF (AMPLITUDE)²
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
10
10
10
10
10
10
10
10
10

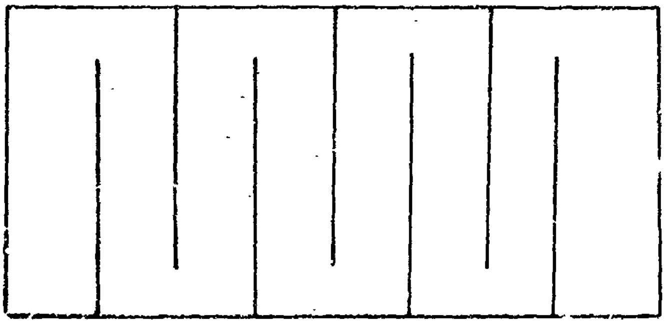


FIG 2.

The platinum serves as a resistance thermometer to measure surface temperature. Some attempts were made to deposit two different metals overlapping to serve as a thermocouple. The resistance thermometer was, however, much easier to deposit and was much more reproducible. The thermocouple idea might still have promise but would require more development than seemed proper in this test.

The sinusoidally varying flux was approached by interrupting the heat radiation from a tungsten filament bulb fitted with internal reflectors. The interruption was by means of a sector disk driven by a variable speed motor.

Since the incident radiation must not be allowed to impinge on the back surface, the front surface (and the back surface) were coated with Black Top #5, an asphalt based black ink which rendered the surfaces opaque. This was found experimentally to be necessary.

The amplitude of the temperature variation on both sides was amplified through a Bogen 200 Amplifier and read on an oscilloscope with calibrated scale. The circuit was as shown in Fig. 3.

The resistance R was chosen to be close to the room temperature resistance of the sample (about 1200 ohms). The filter network was a twin T network designed to filter unwanted 60 cycle pickup.

There was very little time required to reach equilibrium because of the thinness and comparatively high conductivity of the sample.

The points taken from such a test are shown plotted in Fig. 1 using the same ordinates and abcissae as were used in the calculated wave. No corrections of any kind have been applied to these data.

Possible Corrections

Since the incoming flux of radiation is not truly sinusoidal it may be necessary either to carry out a Fourier analysis of the wave form or to arrange a system of electrical filter to transmit only the fundamental frequency.

Corrections will in all probability have to be made for radiation losses from the two faces of the sample. Such losses would change the reflection conditions at the surfaces and would modify the mathematical treatment.

The finite thickness and thermal capacity of the opaque coating might have to be allowed for.

In cases where the sample is very thin it may be desirable to sputter and then electroplate a backing of copper

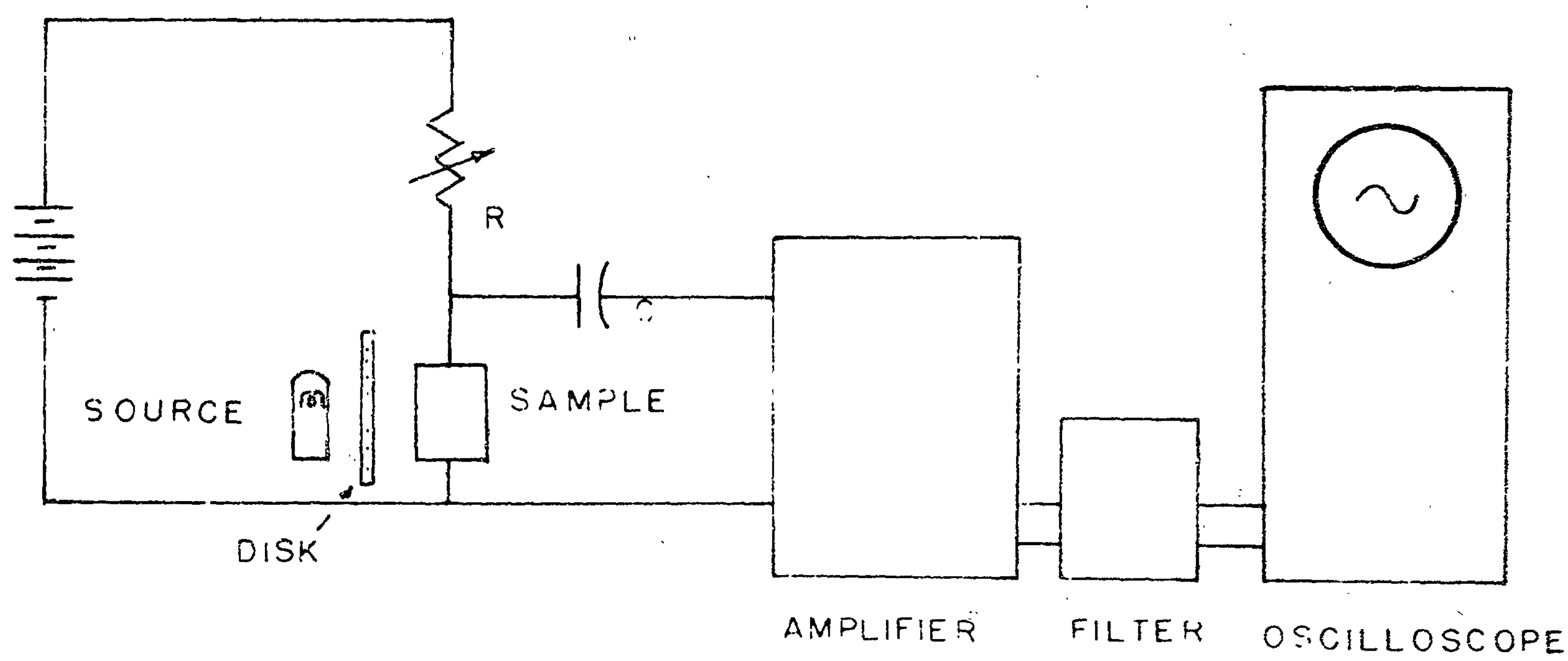


FIG 3

so as to reduce the frequency which may be quite high for thin beryllia samples.

Conclusions

As far as can be judged from these preliminary experiments the method is entirely feasible. Some modifications may have to be made for very thin and very highly conducting samples.

HTS/bjm

January 16, 1964